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Inverse Gas Chromatography study of poly(dimethyl siloxane) - liquid crystal mixtures

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ABSTRACT

Inverse gas chromatographic measurements are reported for seventeen hydrocarbon probes on a low molar mass hexyloxycyanobiphenyl liquid crystal mixed with linear poly(dimethyl siloxane). The retention properties are compared with a side chain liquid crystalline bearing the same mesogen. The results show that the retention of the LC polymer is significantly different from a mixture with the same composition. DSC and IGC values for the transition temperatures indicate that PDMS does not blend with HCB although some interactions, characterised by a Flory-Huggins interaction parameter, were seen and some effect on the liquid crystalline behaviour was noted. The usefulness and limitations of the IGC technique for characterising this type of polymer – LC system are discussed.

INTRODUCTION

Liquid crystal (LC) compounds have found a variety of uses and both low molar mass and polymeric versions have been developed into useful materials¹⁻³. Some applications, such as dyes, coatings and flexible display screens utilise LC's dissolved in a solvent or dispersed in a carrier polymer⁴ and further development of these applications needs detailed knowledge of the interactions between the components. There is also interest in using LC's dispersed in a carrier polymer as analytical chromatography stationary phases. A number of diffraction or scattering methods can be used to study structural features of LC systems.

Inverse gas chromatography, IGC, has been used to investigate the physicochemical properties of a wide range of systems, including polymers^{5,6}. While it is a dynamic method, it was shown some years ago that measurements recorded under the correct conditions could give accurate equilibrium thermodynamic information^{7,8}. The retention of a solvent or "probe" molecule on the material is recorded and the measurements made effectively at infinite dilution of the probe. A range of thermodynamic parameters can then be calculated. One advantage of the method is that it is readily applied to mixtures of two or more polymers. The polymer-polymer interaction parameters χ_{23} between a number of miscible polymer blends have been determined^{9,10}. Early work suffered from the difficulty of determining χ_{23} that was independent of the probes used. This has largely been overcome by suitable experimental protocols¹¹⁻¹³. The methods have also been applied to mixtures of polymers with non-volatile small molecule compounds such as plasticisers^{14,15}.

One of the more commonly used and studied LC systems is the alkyl- or alkoxy-substituted cyanobiphenyls that have been widely used in display applications. Martire and co-workers^{16,17} have studied a series of alkylcyanobiphenyl molecules, characterising them in terms of activity coefficients and the associated enthalpies and entropies associated with the solution process. There have been only relatively few studies of LC polymers, particularly where the mesogen is attached to the polymer in a side chain¹⁸⁻²⁰ or of main chain LCP's, where the mesogen is part of the backbone of the polymer^{21,22}. A comparison of the behaviour of siloxane-substituted cyanobiphenyls with low molar mass equivalents has been reported¹⁹ briefly by Price and Shillcock and the work was extended recently²³ to consider in detail the activity coefficients and interaction parameters of these LC's. It was shown that the interactions in the LCP were governed largely by the mesogen rather than the siloxane polymer backbone. The phase behaviour of an alkylcyanobiphenyl dispersed in PDMS was recently described by Gogibus *et al.*²⁴

This paper presents work aimed at quantifying interactions in LC's dispersed in a polysiloxane fluid. Poly(dimethyl siloxane), PDMS, is unusual in that it has a low glass transition and a very flexible chain. It is also the base polymer for many GC stationary phases. The effect of dispersion on the LC transition temperatures has been examined and PDMS-LC interaction parameters calculated. The behaviour of a mixture of siloxane polymer with a low molar mass LC is also compared with a liquid crystalline polymer with the same overall mesogen composition.

EXPERIMENTAL

Materials. The liquid crystals studied were 4-(n-hexyloxy)-4'-cyanobiphenyl, HCB, and the polymeric poly(dimethyl-co-methyl(4cyanobiphenoxy)butyl siloxane), PDCBBS, which had 40 repeat units. They were supplied by Merck(UK) Ltd with reported purities of 99.5+ %. The structures are shown in Scheme 1 along with the transition temperatures and displayed mesophases reported by the manufacturers. In Scheme 1 and the following discussion, Cr represents the solid, crystalline phase, N and SmA, the nematic and smectic-A mesophases and I denotes the isotropic liquid phase above the clearing temperature. The poly(dimethyl siloxane), PDMS, was fractionated from a DC12500 fluid from Dow Corning and had a number average molecular weight and polydispersity of 24100 and 3.8 respectively as measured by gel permeation chromatography. All probe solvents (Aldrich Chemicals or Merck Ltd.) were 99% pure or better. A total of seventeen probes was used comprising a selection of normal and branched alkanes, cyclohexane, benzene and substituted aromatics.

Differential scanning calorimetry: DSC was performed on a DuPont 3000 calorimeter calibrated with indium and water using a heating rate or cooling of 5 °C min⁻¹ and sample sizes of 4 - 12 mg for pure materials and 15 - 25 mg for the coated materials.

Inverse Gas Chromatography. The stationary phases were prepared on acid washed, silanized Chromosorb P with 100-120 mesh size (Phase Separations). Coating was performed by slurring the LC dissolved in the minimum amount of chloroform with the support followed by removal of the solvent under rotary evaporation. After drying, 1 - 1.5 m lengths of ¼ in o.d. copper tubing which had been washed successively with methanol, acetone and toluene were packed with a known mass of the LC coated support with the aid of a water suction pump and mechanical vibrator. The column was loaded and conditioned for 24 hr at 80 °C under a flow of carrier gas. The amount of LC or polymer on the support was determined by duplicate ashings on about 1 g of material or, for the siloxane materials, by

exhaustive soxhlet extractions of a similar amount of packing with chloroform, accounting for extractable matter from the uncoated support. The loadings used were $14.3 \pm 0.2 \%$ for HCB and $10.0 \pm 0.2\%$ for LCP. Previous work²⁰ has shown that the support does not influence the behaviour of the LC's or of PDMS at this loading.

Measurements were performed on a Carlo Erba 400 chromatograph using oxygen-free nitrogen as the carrier gas and fitted with FID detectors. It was modified to allow accurate measurement of the inlet and outlet pressures across the column. Gas flowrates in the range of $20 - 40 \text{ cm}^3 \text{ min}^{-1}$ were used, adjusted to give retention times with appropriate accuracy. Samples of $\sim 0.01 \text{ }\mu\text{L}$ probe liquid and $0.4 \text{ }\mu\text{L}$ of methane were injected by Hamilton syringe. Where baseline separation was possible several different probes were injected together. Retention times were recorded on a Hewlett Packard 3390A integrator to $\pm 0.01 \text{ min}$. Each of the values reported is the mean of at least three measurements agreeing within $\pm 1 \%$ of the net retention time. Estimation of the marker retention using methane or by extrapolation of the retention of consecutive n-alkanes were in close agreement. The column temperature was monitored to $\pm 0.1 \text{ }^\circ\text{C}$ using a thermocouple that had been calibrated against a Tinsley Type 5840 platinum resistance thermometer. The temperature variation through the oven was less than $0.2 \text{ }^\circ\text{C}$. The usual checks⁶ were made to ensure that the results were independent of sample size and flow rate and that measurements were being made at infinite dilution.

RESULTS AND DISCUSSION

The primary measurement in IGC is the specific retention volume, Vg° , the volume of carrier gas at S.T.P. per gram of stationary phase required to elute the probe²⁵. This is related to the probe retention time, t_R , by

$$Vg^\circ = \frac{(t_R - t_M)F'J}{W} \quad (1)$$

where t_M is the retention time of the methane marker, F' is the carrier flow rate corrected to S.T.P., J is the correction for gas compressibility and W the mass of stationary phase on the column. F' was calculated from the measured flow rate, F , obtained at laboratory conditions and corrected for the laboratory temperature, T , and atmospheric pressure, p_A as well as for water vapour pressure, p_w in the flow-meter using Literature constants²⁶.

$$F' = F \left(\frac{273.15}{T} \right) \left(\frac{760}{p_A} \right) \left[1 - \left(\frac{p_w}{p_A} \right) \right] \quad (2)$$

The correction factor for gas compressibility is given in terms of the column inlet and outlet pressures, p_i and p_o respectively by

$$J = \frac{3}{2} \left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right] \quad (3)$$

The retention diagrams for four illustrative probes in HCB, PDMS and a 60 wt% mixture of HCB in PDMS coated from a common solvent, chloroform, are shown in Figure 1. As expected for a polymer well above its glass transition, the plots for PDMS in Figure 1(a) all gave a linear relationship. HCB gave very different results. On heating the solid, there was a very large change in retention around the melting transition into the nematic phase and a second break in the plot occurred at the N - I phase change. The phase transition temperatures correlate well with those measured by other methods²⁰. On cooling from the isotropic liquid, shown by the solid points in Figure 1(b), there was considerable hysteresis and a supercooled N phase exists below the equilibrium freezing point. These factors have been investigated and commented on previously²⁰.

Figure 1(c) shows the retention diagram for a stationary phase coated from a solution of HCB and PDMS in a common solvent. It is clear that the LC retains the major features of Figure 1(b) and that its behaviour was similar to that in the pure component. Note that the retention volumes are calculated per gram of stationary phase and so the smaller change in V°_g on melting is simply due to the lower proportion of HCB. For clarity and brevity, only four probe molecules have been included in the Figure but all seventeen yielded essentially the same results.

If the LC were simply phase separated and dispersed in the PDMS the retention volumes of the two components would be expected to be additive and to show a linear variation with composition²⁷. Figure 2 shows how the specific retention volume for two probes, hexane and benzene, varied as the ratio of HCB and PDMS was changed. Clearly those for the mixed stationary phases do not follow a linear relation in the middle of the range implying that there was a contribution to retention from interactions between the two components and that they did not act totally independently. At the lower temperatures, where the cyanobiphenyl will be in its mesophase, the behaviour is close to linear but the deviation is more significant at the high temperatures where it will be an isotropic liquid. Again, the other probes investigated yielded very similar results.

It is interesting to compare the V°_g for the mixed phases with those of a polymer with the same composition. Figure 3 shows the retention diagram for a cyanobiphenyl substituted

siloxane, PDCBBS. Again the change in retention on passing through the mesophase transition is clear. From its composition (confirmed by ^1H nmr spectroscopy), the polymer contained effectively 62 wt% of the mesogen. The retention volumes at this composition are also shown in Figure 2 and are considerably lower than those for the binary stationary phases. This reflects the structure of PDCBBS where the mesogen and polysiloxane backbone are compelled to interact more intimately than the individual components, HCB and PDMS. Note that the mesophase in the PDCBBS is a smectic phase compared with the nematic in HCB. In related work,^{20, 28} cyanobiphenyls which display SmA phases were found to have only small differences from N phases at the same temperature so that the different mesophase structure would not account for the differences reported here.

If PDMS formed a true blend with HCB, it would be expected that melting and mesophase transition temperatures of the LC would be lowered from those of the pure components. By analogy with the determination of melting temperatures in semi-crystalline polymers, the retention diagrams above were used to measure the transition temperatures of the mixtures. Previous work²⁰ has confirmed the validity of IGC for determining LC transitions. For comparison, the temperatures were also measured by DSC where the coated material used for IGC was investigated. Independent samples were prepared by casting mixtures from a common solvent directly into the DSC pan so that any effect of the chromatography support could be ascertained.

Figure 4 shows the results obtained from both IGC and DSC. Each point is the result of duplicate runs agreeing to within ± 1 °C. Results from both coated and uncoated samples are in reasonable agreement with some discrepancy in values at low HCB compositions. This seems likely to be an artefact since any interaction of the LC with the support would be expected to lower the clearing temperature. The values for coated materials measured by IGC and DSC in very good agreement across the composition range. For the Cr - N transition there was no significant composition dependence.

These results suggest that the PDMS has negligible effect on the melting (Cr - N) transition confirming that there is no disruption of the LC structure in the solid phase and that the two components are, as expected, immiscible. However, it was noticeable that the melting occurred over a smaller range of temperature at lower HCB concentrations. This may indicate that in the presence of PDMS, smaller crystallite regions are present than would be the case in the pure component. There is a small effect on the N - I clearing temperatures but this was too small to be a result of strong blending interactions between the two components.

In systems where two similar LC's interact strongly and form a eutectic, the clearing temperature is usually unaffected while the melting temperature exhibits a characteristic dip²⁹. There is some disagreement between the bulk and coated results measured by DSC with the unsupported systems giving lower transition temperatures. Gogibus²⁴ *et al.* have reported similar results using polarised microscopy in the PDMS – pentylcyanobiphenyl system. They reported that the transition started at lower temperatures with decreasing amounts of HCB but ended at the same temperature irrespective of composition. The discrepancy in DSC results may be due to there being less HCB in the coated samples so that effects would be less apparent. The IGC results would report the higher of these values due to the method of data interpretation since the reported temperatures are the highest temperatures before isotropic equilibrium retention begins.

The interaction between two components in a mixture can be quantitatively assessed using an extension of the Flory-Huggins approach in terms of the interaction parameter between the components of the stationary phase, χ_{23} . The method is not without difficulties since the values of χ_{23} often depend on the probe used although more recently these have been overcome by suitable data treatment. The two components do not have to interact favourably, but the mixture should be reasonably homogenous for the theory to be applicable and the probe must interact with all of the individual components. In this work, there is some question as to whether the mixed components meet this criterion. If the two components were completely miscible, the mesophase behaviour would be lost at high PDMS composition. This does not occur but partial inclusion of PDMS within the mesophase is a possibility and calculating the interaction parameter on the basis of assuming an homogenous system will allow an evaluation of the plausibility of such a model.

For the interaction of a probe, denoted component 1, with a single component stationary phase, denoted 2, the interaction parameter, χ_{12}^{∞} , can be calculated from the specific retention volume, V_g° , by:

$$\chi_{12}^{\infty} = \ln \left(\frac{273.15 R v_2}{V_g^{\circ} p_1^{\circ} V_1^{\circ}} \right) - \left(\frac{p_1^{\circ} (B_{11} - V_1)}{RT} \right) - \left(1 - \frac{V_1^{\circ}}{V_2^{\circ}} \right) \quad (4)$$

where V_1° , B_{11} and p_1° are respectively the molar volume, the second virial coefficient and the saturated vapour pressure of the probe vapour at the column temperature T and v_2 is the specific volume of the polymer. The superscript $^{\infty}$ denotes that the measurements are made at

infinite dilution. In calculating the interaction parameters reported, pure component data were taken from reliable Literature sources^{26, 30-32}.

Extension to a two component stationary phase involves calculation of the interaction parameter of the probe with the binary stationary phase, $\chi_{1(23)}^\infty$,

$$\chi_{1(23)}^\infty = \ln \left(\frac{273.15R(w_2v_2 + w_3v_3)}{V_g^\circ p_1^\circ V_1^\circ} \right) - \left(\frac{p_1^\circ(B_{11} - V_1)}{RT} \right) - \left(\phi_2 \left(1 - \frac{V_1^\circ}{V_2^\circ} \right) + \phi_3 \left(1 - \frac{V_1^\circ}{V_3^\circ} \right) \right) \quad (5)$$

where w and ϕ are the weight and volume fractions of the two stationary phase components.

From this, and the interaction parameters for the pure components, χ_{12}^∞ and χ_{13}^∞ , the value of χ_{23} can be then found from

$$\chi_{1(23)}^\infty = \phi_2 \chi_{12}^\infty + \phi_3 \chi_{13}^\infty - \phi_2 \phi_3 \chi_{23} \left(\frac{V_1^\circ}{V_2^\circ} \right) \quad (6)$$

The probe dependence of χ_{23} has been tackled in a variety of ways. One method is to quote an average of values obtained for a range of probes although this is not very satisfactory. These approaches were reviewed by Farooque and Deshpande³³ who introduced a simplified method for overcoming this problem by rearranging Equation (6)

$$\frac{(\chi_{1(23)}^\infty - \chi_{13}^\infty)}{V_1^\circ} = \left(\frac{\phi_2(\chi_{12}^\infty - \chi_{13}^\infty)}{V_1^\circ} \right) - \left(\frac{\phi_2 \phi_3}{V_2^\circ} \right) \chi_{23} \quad (7)$$

A plot of the left hand side versus $(\chi_{12}^\infty - \chi_{13}^\infty)/V_1^\circ$ yields a linear function from which χ_{23} can be found from the intercept. This treatment found to give better interpretation of the polystyrene-polybutadiene system than other, somewhat more rigorous, arguments.

The interaction parameters for the two pure components are shown in Figure 5. These have been reported and fully discussed previously²⁸. Probe-binary stationary phase interaction parameters were calculated from the retention volumes exemplified by Figure 1(c). The results for seventeen probes used in this work were applied in Equation (7) and gave the result shown in Figure 6. There was a good linear correlation for the data and the normalised χ_{23} for each mixture of PDMS and HCB are shown in Table 1. The standard error of the values was relatively high showing that this method of data treatment is not without problem but it does allow identification of some trends in the data.

The slope of the plots in Figure 6 gives the effective volume fraction of the HCB component of the stationary phase that the probe samples. The values are shown in Figure 7 along with the value predicted if all the mixture were sampled. In the isotropic phase there was good agreement suggesting that the solvent probed all the liquid crystal component. In

the nematic mesophase the sampled volume fraction decreased at lower temperatures and the effect became more prominent as the proportion of PDMS increased. This indicates the probe was preferentially dissolving in the polymer. However, the majority of the HCB component was apparently sampled for all systems and values will approach the true interaction parameter as the temperature is raised and the composition of HCB increased.

The variation of χ_{23} with temperature and composition is summarised in Figure 8. There was a maximum in χ_{23} at each temperature investigated as the composition changed. In principle, this parameter should be constant with composition but has often been found to show significant variations. The results here show that the straightforward solution model employed cannot satisfactorily account for the observed behaviour. The values of χ_{23} suggest that the interactions become more unfavourable as the amount of HCB or PDMS increased in the stationary phase. They were lower for the N phase suggesting that it was more compatible with PDMS but this may be a consequence of the reduced fraction of the HCB phase the solvent was probing. In addition, χ_{23} increased with temperature. In particular, the negative values for the N phase at the high compositions indicate strongly favourable interactions between the components and are difficult to rationalise on any physically reasonable description of the system.

Further discussion

The data suggest that unfavourable interactions between HCB and PDMS occurred toward the centre of the composition range but that some solubility of the components was achieved at the extremes. The high values of χ_{23} suggest that they are largely incompatible. However, this is somewhat at odds with the retention data of Figure 2 which suggested that the components did not act completely independently at the middle compositions.

The implication arising from the results is that fluid phases of HCB can interact with PDMS at certain compositions. A possible explanation for the results is that the size of the HCB crystallite regions plays an important role in the phase behaviour. If the two components act independently, the crystalline region would be little affected by the polymer and the melting temperature would remain constant as the composition of the solution changed. However, the mesophase could be constrained by the surrounding polymer. As the crystallites become smaller this effect becomes more pronounced leading to the clearing temperature rising as the PDMS fraction increased. Considering the effects of crystallite size and any interactions it is possible to rationalise the observed behaviour as the result of these

competing effects. At higher levels of HCB, the governing effect is the interaction between components. The expected lowering of the clearing temperature as the PDMS fraction increased was compensated for by the decreasing interaction. At the other end of the composition scale, the size of the mesoscopic regions may be sufficiently small for this to be the governing factor. This picture is consistent with the observed interaction parameter data. However, these must remain preliminary conclusions and further investigation is needed before the behaviour of this binary stationary phase is fully elucidated.

DSC and IGC values for the transition temperatures indicate that PDMS does not blend with HCB and does not affect the melting temperature. However, as the composition of PDMS increased, the HCB phase appeared to form smaller crystallites. Although the solid, crystalline HCB phase separates from PDMS and this calls into question the interpretation of the results, the interaction parameters between PDMS and HCB suggest that there is some favourable interaction between the fluid liquid crystal phases with PDMS at low compositions.

CONCLUSIONS

The results show that IGC can be used to obtain information about binary stationary phase solutions containing liquid crystals. However, any quantitative information must remain open to question and interpretation and IGC data, particularly using simple models of mixed solution behaviour is not sufficient for a full description or characterisation in the absence of information from other experimental methods. The brief study of separation properties of binary HCB-PDMS stationary phases shows that the retention of a LC polymer is significantly different from a mixture with the same composition. This has implications for the analytical use of PDMS dispersed LC's. DSC and IGC values for the transition temperatures indicate that PDMS does not blend with HCB and does not affect the melting temperature. However, as the composition of PDMS increased HCB appeared to form smaller crystallites. Although the crystalline HCB phase separates, the interaction parameters between PDMS and HCB indicate that the fluid liquid crystal phases do interact with PDMS.

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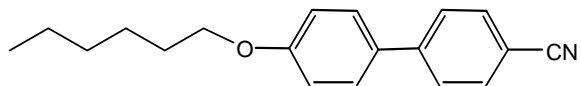
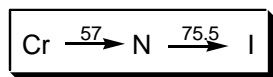
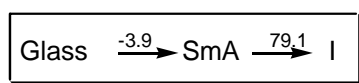
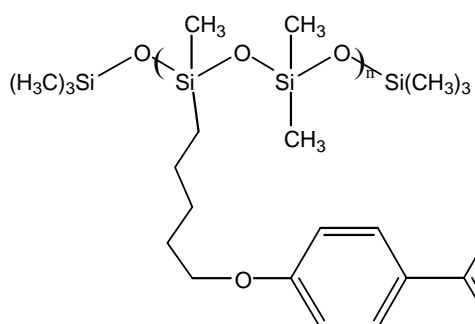
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Table 1: Interaction parameters, χ_{23} , between HCB and PDMS. (standard error of the values in parentheses).

		HCB:PDMS ratio by mass*			
Temperature /°C	HCB Phase	80:20	60:40	40:60	20:80
90.0	Isotropic	0.57 (0.21)	1.57 (0.32)	2.01 (0.21)	0.62 (0.33)
85.0		0.45 (0.50)	1.41 (0.98)	1.81 (0.55)	0.41 (0.98)
80.0		0.38 (0.21)	1.48 (0.34)	1.62 (0.17)	0.16 (0.35)
72.0	Nematic	0.12 (0.11)	1.71 (0.26)	1.34 (0.25)	-0.42 (0.30)
70.0		-0.01 (0.12)	1.43 (0.26)	1.33 (0.21)	-0.52 (0.24)
65.0		0.11 (0.15)	1.23 (0.24)	1.30 (0.21)	-0.64 (0.20)
60.0		0.13 (0.14)	1.29 (0.27)	1.00 (0.19)	-0.77 (0.16)

* composition reported as mass percentages

Scheme 1

4-(n-hexyloxy)-4'-cyanobiphenyl, **HCB**poly(dimethyl-co-methyl(4cyanobiphenyloxy)butylsiloxane), **PDCBBS**

CAPTIONS FOR FIGURES

Figure 1: Representative retention diagrams for PDMS, HCB and 60:40 mixture of HCB:PDMS as a function of temperature. Solid points recorded on heating; open points recorded on cooling.

Figure 2: Retention volumes at the indicated temperatures (°C) of PDMS:HCB mixtures for (a) hexane and (b) benzene probes.

Figure 3: Retention diagram for four probes in PDCBBS liquid crystal polymer

Figure 4: Liquid crystal transition temperatures versus HCB composition measured by IGC and DSC (coated and uncoated material).

Figure 5: Flory Huggins interaction parameters for probes in (a) HCB and (b) PDMS.

Figure 6: Deshpande-Farooque at 90 °C plots to calculate χ_{23} for HCB:PDMS mixtures with the indicated compositions.

Figure 7: Effective volume fraction of HCB measured from the Deshpande-Farooque method. The lines represent the calculated volume fraction predicted from the prepared wt% composition shown in the legend.

Figure 8: Interaction parameters between PDMS and HCB stationary phase components at the indicated temperatures (closed points, Isotropic HCB, open points, Nematic HCB mesophase)

Figure 1: Representative retention diagrams for PDMS, HCB and 60:40 mixture of HCB:PDMS as a function of temperature. Solid points recorded on heating; open points recorded on cooling.

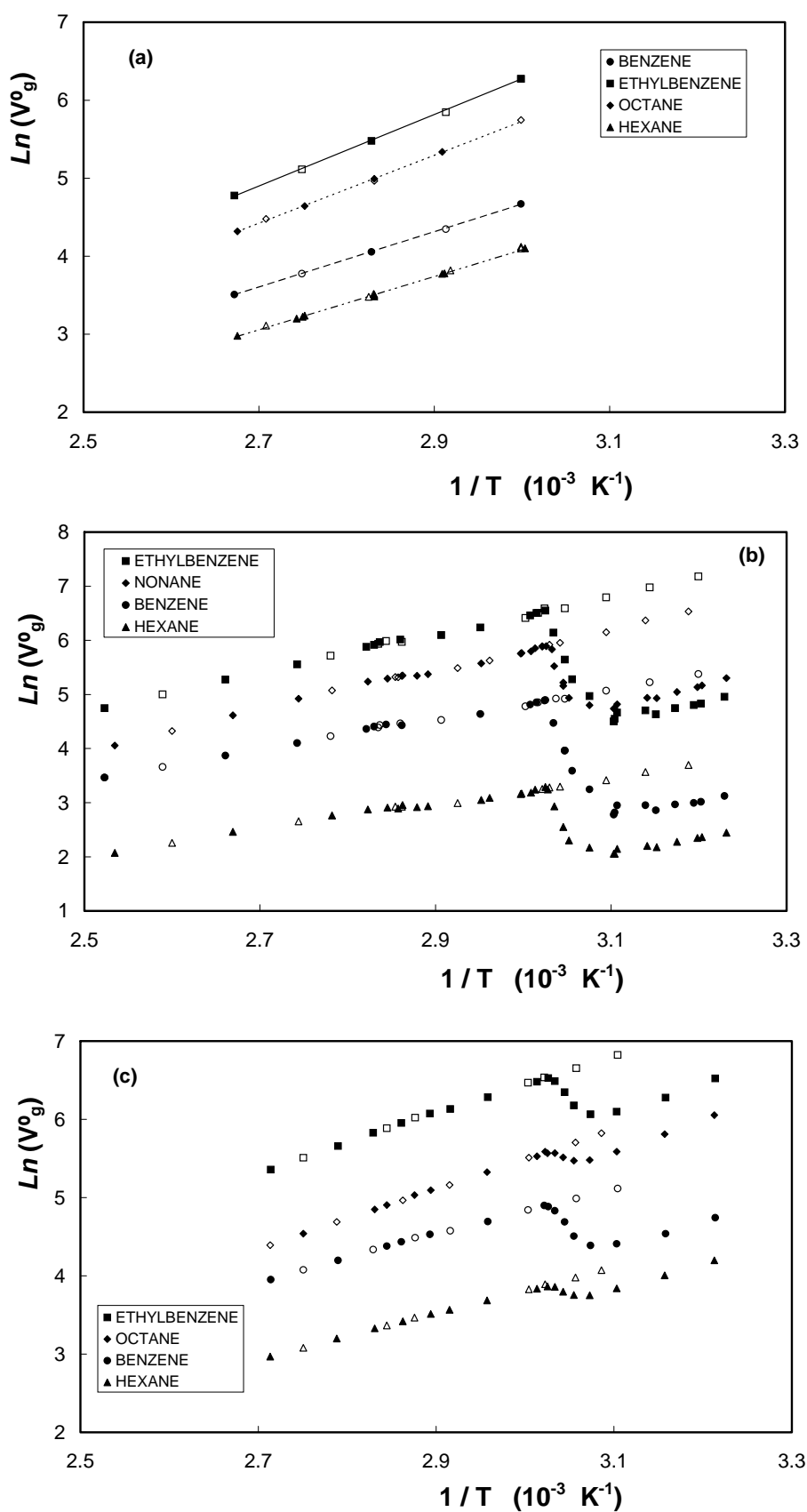


Figure 2: Retention volumes at the indicated temperatures (°C) of PDMS:HCB mixtures for (a) hexane and (b) benzene probes.

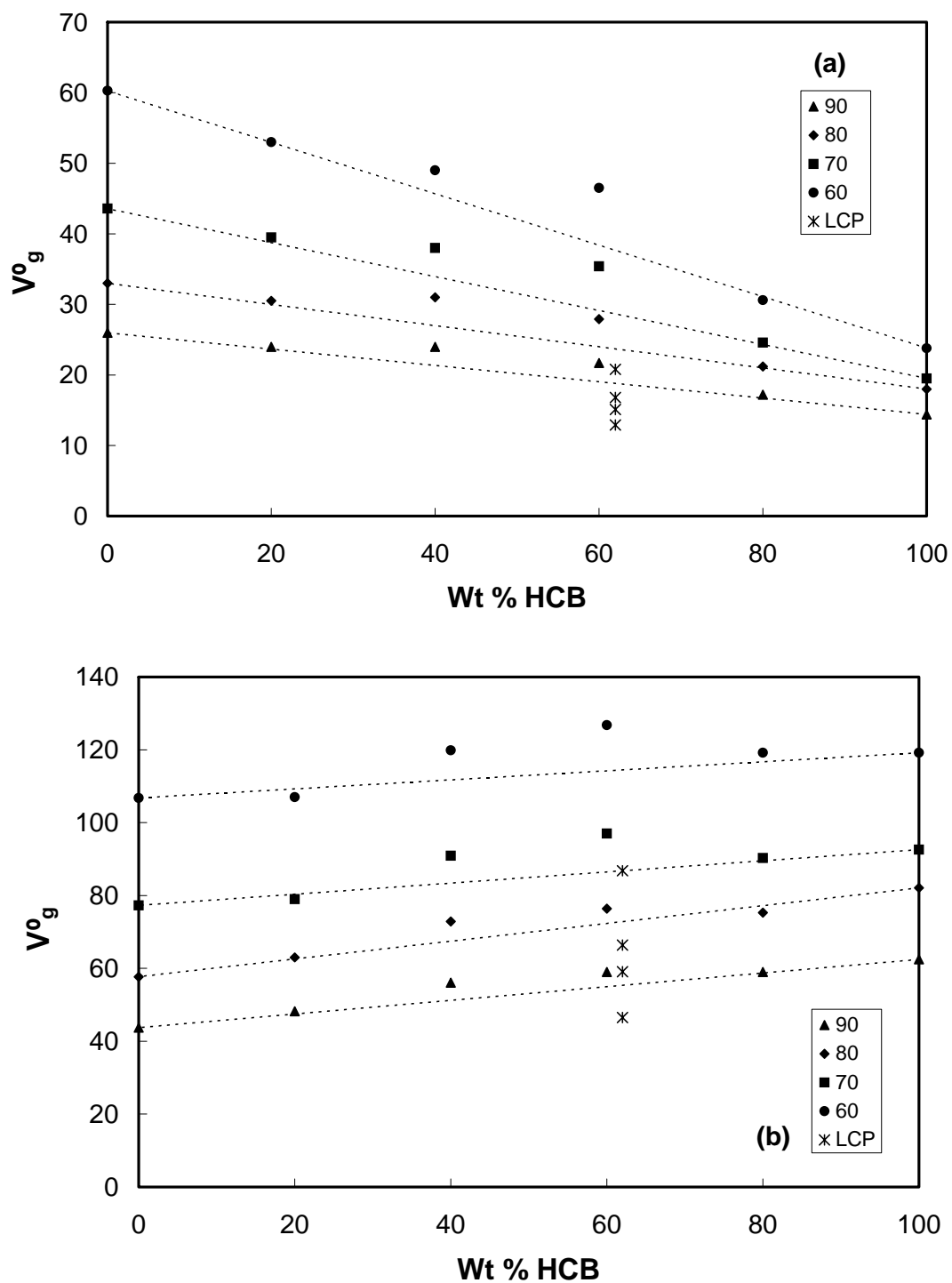


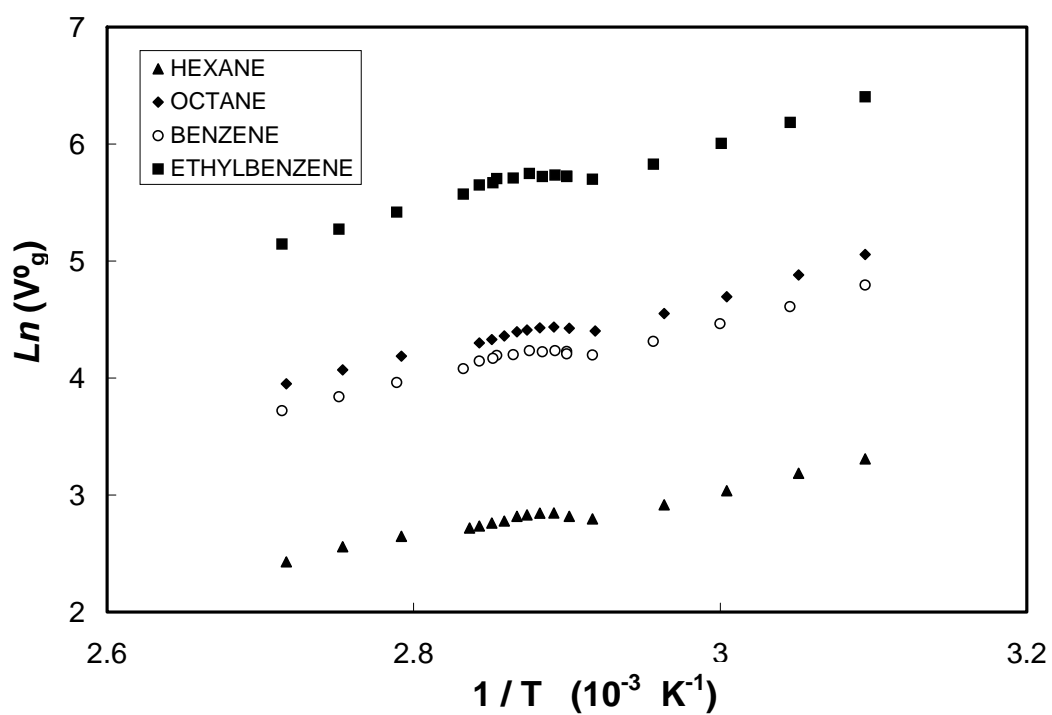
Figure 3: Retention diagram for four probes in PDCBBS liquid crystal polymer

Figure 4: Liquid crystal transition temperatures versus HCB composition measured by IGC and DSC (coated and uncoated material).

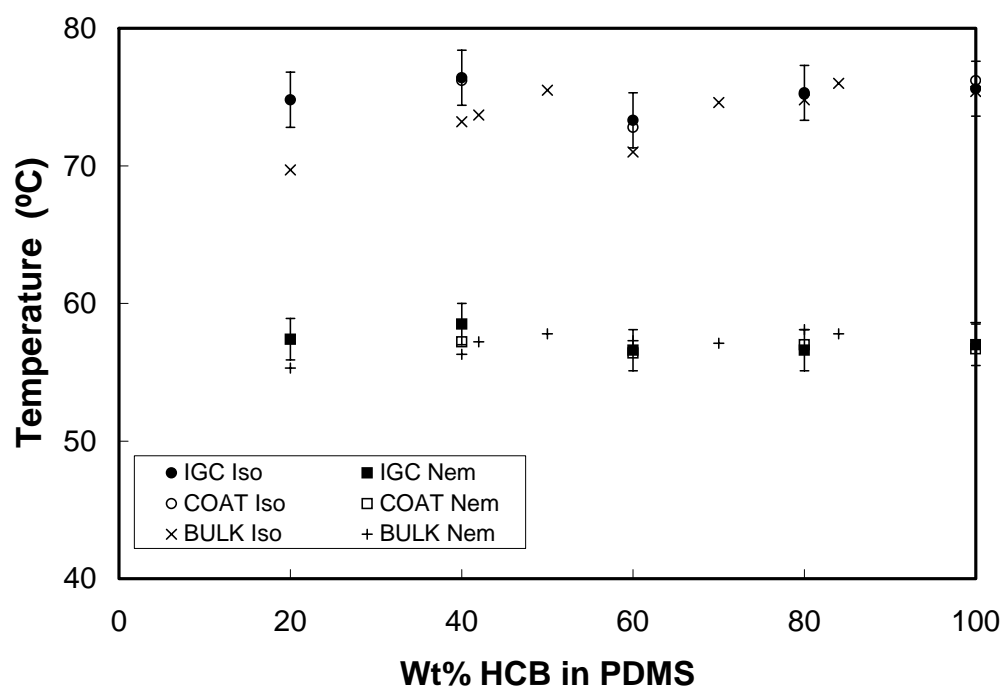


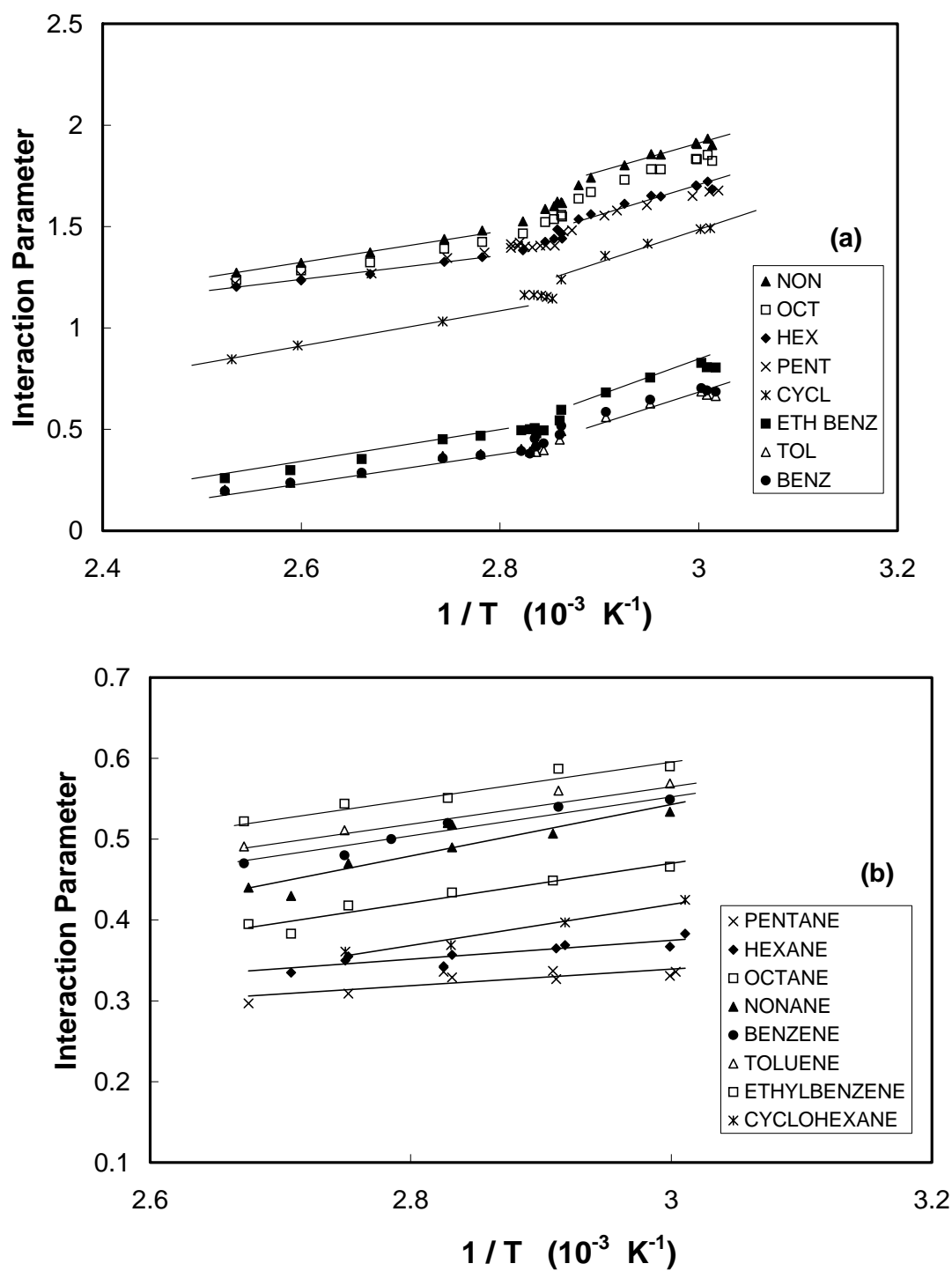
Figure 5: Flory Huggins interaction parameters for probes in (a) HCB and (b) PDMS.

Figure 6: Deshpande-Farooque at 90 °C plots to calculate χ_{23} for HCB:PDMS mixtures with the indicated compositions (wt% HCB).

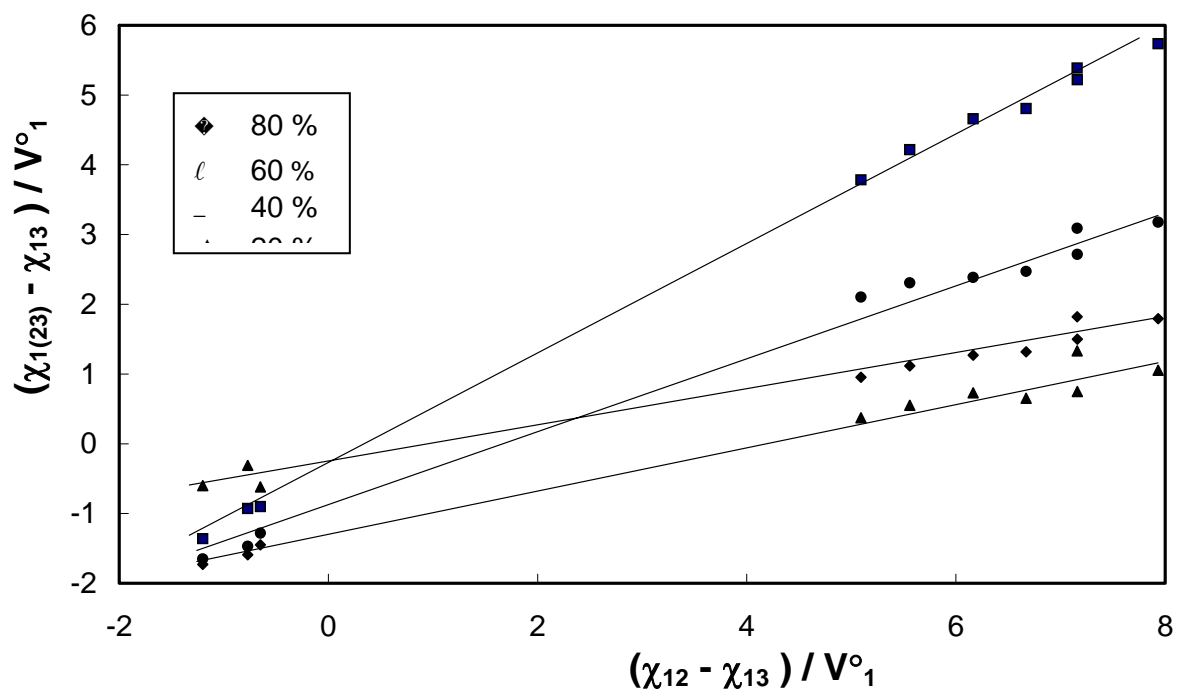


Figure 7: Effective volume fraction of HCB measured from the Deshpande-Farooque method. The lines represent the calculated volume fraction predicted from the prepared wt% composition shown in the legend.

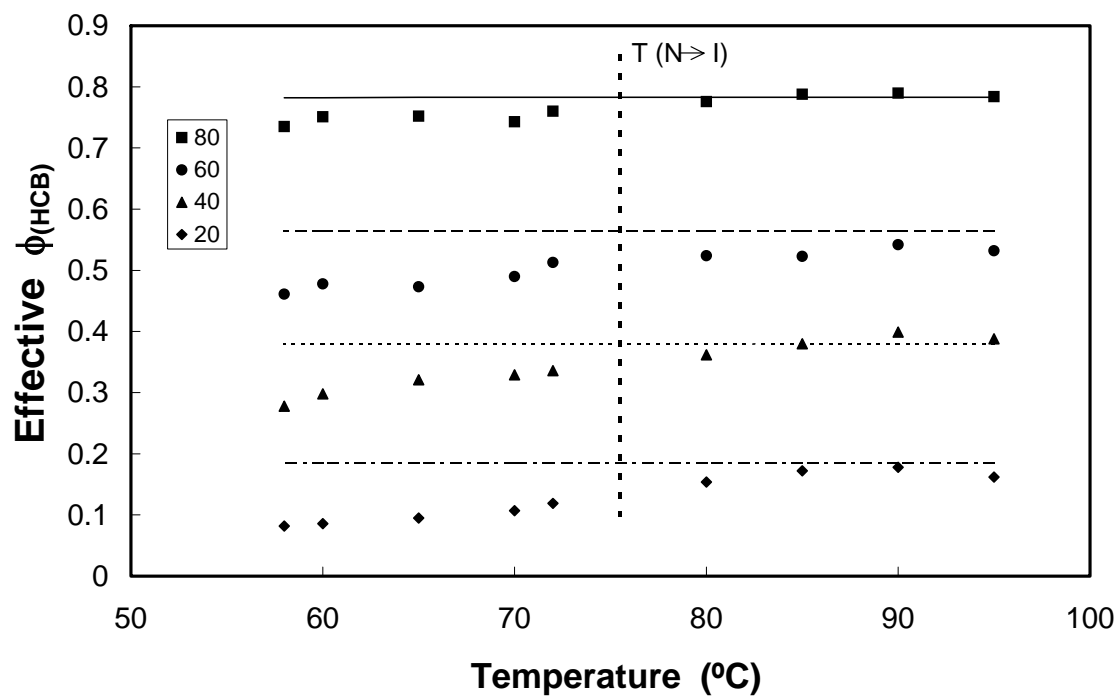


Figure 8: Interaction parameters between PDMS and HCB stationary phase components at the indicated temperatures (closed points, Isotropic HCB, open points, Nematic HCB mesophase)

